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X-RAY FLUORESCENCE ANALYSIS FOR BARIUM ZINC CALCIUM AND  
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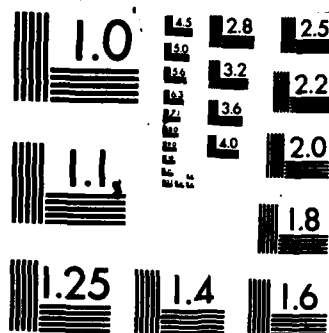
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**MRL-TN-475**

**X-RAY FLUORESCENCE ANALYSIS FOR BARIUM, ZINC,  
CALCIUM AND PHOSPHORUS IN OIL ADDITIVES**

W.B. Searle\*

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## DOCUMENT CONTROL DATA SHEET

REPORT NO.  
MRL-TN-475AR NO.  
AR-003-796REPORT SECURITY CLASSIFICATION  
UNCLASSIFIED

## TITLE

X-RAY FLUORESCENCE ANALYSIS FOR BARIUM, ZINC,  
CALCIUM AND PHOSPHORUS IN OIL ADDITIVES

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REPORT DATE  
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CLASSIFICATION/LIMITATION REVIEW DATE

CLASSIFICATION/RELEASE AUTHORITY

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## KEYWORDS

X-RAY FLUORESCENCE

CHEMICAL ANALYSIS  
OILS  
PETROLEUM PRODUCTS  
ADDITIVESBARIUM  
ZINC  
CALCIUM  
PHOSPHORUS

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A thin film dilution technique is described for the determination of barium, zinc, calcium and phosphorus in oil additives using x-ray fluorescence spectrometry. The specimen was drawn into a thin film by means of a wire wound metering rod. An internal standard was used to compensate for variations in the overall film thickness. The accuracy and repeatability were determined by comparison with chemical results. The agreement obtained between x-ray and chemical results on a wide variety of samples showed that the thin film technique adequately compensated for inter-element effects. The limits of detection were 0.01% Ba, 0.02% Zn, 0.04% Ca and 0.01% P.

Barium

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X-RAY FLUORESCENCE ANALYSIS FOR BARIUM, ZINC,  
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1. INTRODUCTION

Oil additives based on four elements barium, zinc, calcium and phosphorus are employed to enhance certain properties of modern lubricating oils. The quantitative x-ray emission analysis of additives is complicated by the extreme variations in their physical and chemical composition. In recent years tedious and time-consuming wet chemical analyses for barium, zinc and calcium in oils have largely given way, in routine analysis, to spectroscopic methods. A major disadvantage of atomic absorption spectroscopy is its inability to analyse for phosphorus. Wet chemical techniques are used for phosphorus determinations.

Cummins and Mason [1] report the application of a direct reading spectrograph (a rotating anode method) to the determination of barium, phosphorus, calcium and zinc in "neat additives". They studied the effects of:

- (1) viscosity,
- (2) inter-element interference, and
- (3) additive type.

on the line intensities of each element. Their method required the analysis of a "standard containing all four elements in the same viscosity grade as the sample." In cases where the sample nature was unknown an "infra-red examination will establish the additive type". By this means the authors were able to "correctly select which calibration was to be used".

X-ray fluorescence analysis has been used extensively in the field of oil analysis. Absorption and enhancement effects cause variations in the intensity of the analyte-line radiation and thereby complicate the accurate quantitative analysis of elements commonly found in additives and lubricating

oils. Various techniques have been devised to overcome these difficulties and include:

- (1) the direct comparison with a chemically analysed standard having a similar composition as the sample.
- (2) dilution of the sample with a base stock. (In some instances a ten fold or more dilution with base stock may be required so that the concentration of the element sought lies within the linear calibration range of the instrument), and
- (3) the internal standard method.

These procedures have not always been successful when the determination of several elements was sought in a wide variety of samples. The main disadvantages of the comparison standard approach are that prior knowledge of the additive type is required and a comprehensive range of chemically analysed standards to cover all possibilities of concentration variations must be on hand. Davis and Van Nordstrand [2] analysed for barium, zinc and calcium in lubricating oils and applied correction factors to correct for inter-element effects. They claimed "accuracies within 2 or 3% of barium or calcium when present in concentrations greater than 0.05% and within 1 to 2% of zinc in concentrations greater than 0.005%".

The usefulness of the internal standard technique in minimising interelement effects was demonstrated by Louis [3,4] who showed that the best practical approach to the accurate determination of barium, calcium, zinc and phosphorus in lubricating oils was the use of several internal standards, appropriate to the elements sought. Burke et al. [5] adopted the internal standard method for the determination of lead, barium, zinc and calcium in lubricating oils in the range of 0-1% m/m. Haycock [6] discussed the advantages of the internal standard technique for the determination of barium in additives and zinc and calcium analyses in lubricating oils and claimed "precisions equal or superior to those from chemical methods".

The main limitation associated with the internal standard technique is the availability of the element in an oil soluble form. The choice of an internal standard is further limited since similar absorption and enhancement effects should be experienced by both the element sought and the internal standard element. Ideally the two analyte lines to be measured must be on the same side of the absorption edge of the sample components and should be very close in wavelength. Some examples of useful internal standards which have been employed are listed in Table 1. Their relative positions in the x-ray wavelength spectrum are illustrated in Fig. 1. It will be noticed that:

- (1) the elements zirconium and phosphorus represent an ideal combination in terms of the selection requirements for an internal standard element and the element sought, and



- (2) the combination of calcium K $\alpha$  and tin L $\beta$  is unsuitable [7]. (These lines cannot be sufficiently resolved to be useful over the desired calcium concentrations.)

The thin film technique was used by McGinness, Scott and Mortensen [10] for the quantitative x-ray emission analysis of paints. The paint films, "one-half mil dry film thickness", were prepared using a Gardner Ultra applicator. They used copper, in the form of copper naphthenate, as an internal standard. Recent applications of the thin film technique have involved the determination of sulphur in oil. Bauer, Corbyn and Green [11] used a thin layer solidified with paraffin wax to determine sulphur in oil. They obtained accurate and reproducible results for sulphur contents less than 3% m/m. Searle [12] has applied the thin film technique to the determination of sulphur in oil using a K Hand Coater to convert the sample into a thin film. The method used an internal standard to compensate for variations in specimen thickness.

A rapid method was needed to overcome the inconvenience of some of the above procedures. This paper describes a technique whereby the sample mixture, consisting of additive, alkyd resin and zirconium octoate, is converted into a thin film by means of a wire wound metering rod, a K Hand Coater, K Bar No. 3. The specimen is then analysed in the form of a thin film and only one sample preparation is required.

## 2. EXPERIMENTAL

### 2.1 Reagents

Barium additive : An oil additive containing 13% m/m barium.\*

Zinc additive : An oil additive containing 12% m/m zinc.\*

Calcium additive : An oil additive containing 7% m/m calcium.\*

Phosphorus additive : An oil additive containing 9% m/m phosphorus.\*

Conostan Standards : Certified barium, zinc, calcium, and phosphorus concentrates.<sup>+</sup>

Internal Control Standard : 6% m/m Zirconium as zirconium octoate in white spirit.<sup>++</sup>

Alkyd Resin Mixture : Beckosol (50-003) diluted 1:1 with white spirit (barium, zinc, calcium and phosphorus free).<sup>++</sup>

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\* Lubrizol Aust. Pty Ltd.

+ Continental Oil Co., Ponca City, OK, USA

++ Available from A.C. Hatricks Chemicals Pty Ltd.

## 2.2 Apparatus

The measurements were carried out on a Philips PW1540 manual spectrometer with a PW1010 generator. A helium path was used for all determinations and the operating parameters are given in Table 1. The sample was drawn into a thin film on a 25  $\mu$ m Mylar substrate using the K Hand coater.

## 2.3 Preparation of Calibration Standards

The appropriate amount of the above additive, (or Conostan concentrate), was diluted with the alkyd resin so that the concentration of each element was within the range of: 0-15% Ba, 0-12% Zn, 0-7% Ca or 0-9% P.

## 2.4 Preparation of Films

Standards and samples were prepared similarly by weighing 5.00 g of additive and 4.00 g of the internal control standard into a 25 ml capacity glass stoppered bottle. Approximately 10 ml of the alkyd resin solution was added and the contents thoroughly shaken to ensure homogeneity.

A portion of the mixture was poured onto the Mylar sheet and drawn into a thin film using the K Hand Coater. A disc was cut from a central area of the film and mounted in the x-ray sample cup so that the sample film was closest to the x-ray target. Duplicates were prepared from each sample.

## 2.5 Calibration Curves

The intensities of the additive element sought and zirconium were measured, their ratio calculated and plotted against the known chemical concentration of the additive element. The calibration curves were found to be linear throughout the desired concentration range. The intensity measurements were corrected to the time of analysis by means of a suitable external reference standard to compensate for fluctuations in instrumental sensitivity on a day-to-day basis. Owing to the unstable nature of the zirconium standard it was necessary to recalibrate after approximately 2-3 weeks.

# 3. ANALYTICAL RESULTS

At the time of analysis it was not possible to carry out quantitative analyses on all of the oil additive samples for barium, zinc, calcium and phosphorus in accordance with the Institute of Petroleum (IP) Standard Methods for Testing Petroleum and its Products (Part 1 Methods for Analysis and Testing). The reported wet chemical analytical results were determined using different wet chemical techniques. Checks on the accuracy of the thin film method were made by comparing the XRF results with those

obtained by the wet-chemical method (Table 3). While the accuracy of the XRF method cannot be absolutely shown the agreement between the XRF and wet-chemical methods was satisfactory.

The precision of the method was estimated by a series of six determinations for barium, zinc, calcium and phosphorus on eight different oil additives. The standard deviation ( $2\sigma$  value) and the coefficient of variation, reported for two concentrations of each element, are given in Table 4. The values obtained from this test include not only the error of counting measurements on a sample and standard but also the errors caused by any sample variations introduced during preparation of the mixtures. It can be seen that the method has good precision.

The analyte-line intensity recorded from a thin film is affected by the thickness of the hydrocarbon film. If the film is thin enough then the measured intensity will be proportional to the concentration of the element sought. Alternatively x-ray absorption causes a marked reduction in the analyte-line intensity measured using bulk specimens and results from the nature of the hydrocarbon blend as well as the thickness of the Mylar film used to contain the sample to be analysed in the standard Philips sample cup. Table 5 lists the intensity data recorded from the thin film specimens. The sensitivity of x-ray fluorescence recorded for each element of interest in the thin film was found to be adequate for useful analysis. The x-ray spectroscopic limit of detection improves with sensitivity and is dependent upon the background intensity where, in particular, substrate impurities give rise to interfering lines near the analytical line. The limits of detection values given in Table 5 were estimated using three standard deviations of the background intensity measured on a "blank". The thin film procedure will give poorer limits of detection as compared to bulk specimens.

#### 4. CONCLUSION

The proposed analytical technique permits the determination of barium, zinc, calcium and phosphorus in oil additives over a wide concentration range without significant interelement effects. The accuracy and precision of the thin film method were comparable with wet chemical methods. The thin film technique is rapid, simple and more versatile than conventional x-ray methods and would be particularly useful for routine analysis in the oil industry.

#### 5. ACKNOWLEDGEMENT

The author wishes to acknowledge Mr E.S. Sharkey for the wet chemical determinations. Mr A.H. Kingsbury is thanked for providing the samples and the remaining chemical results. Dr G.L. Wulf is also thanked for his assistance given in the preparation of the paper.

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T A B L E 1

Examples of Internal Standards for Oil Additives Elements

Additive element	X-ray line	Wavelength A	Absorption edge, A	Internal standard	X-ray line	Wavelength A	Absorpt edge,	Ref
Barium	L $\alpha$	2.775	2.363	L $\alpha$	L $\alpha$	2.665	2.258	5,9
Barium	L $\beta$	2.567	2.363	Cr Mn	K $\alpha$ K $\alpha$	2.291 2.104	2.070 1.896	6 3,4
Zinc	K $\alpha$	1.437	1.283	Cu Bi	K $\alpha$ L $\alpha$	1.542 1.144	1.380 0.923	4,5 5
Calcium	K $\alpha$	3.360	3.070	Sn Sn Sb	L $\alpha$ L $\beta$ L $\alpha$	3.600 3.385 3.439	3.146 3.146 3.000	4 8 5
Phosphorus	K $\alpha$	6.155	5.787	Zr	L $\alpha$	6.070	5.583	3,4

T A B L E 2

X-ray Spectrometer Parameters

Element	Barium	Zinc	Calcium	Phosphorus	Zirconium	
X-ray line	La	Ka	Ka	Ka	Ka	La
Analysing crystal	LiF	PE	PE	PE	LiF	PE
X-ray line setting, 2 $\theta$	87.14	41.81	45.11	89.28	22.57	87.72
Detector	FC	FC	FC	FC	SC	FC
Atmosphere	He	He	He	He	He	He
Tube voltage, kV	50	50	50	50	50	50
Tube current, mA	18	18	18	18	18	18
Collimation, $\mu$ m	160	160	160	480	160	480
Counting time, sec	100	100	100	100	100	100
Pulse height analyser	yes	yes	yes	yes	yes	yes

Detectors : SC - scintillation counter  
: FC - flow counter with P10 gas (10% methane in argon)

Analysing Crystals : LiF - lithium fluoride (200)  
: PE - pentaerythritol

T A B L E 3

Comparison of X-ray and Chemical Analytical Data for Oil Additives

Sample	Other* Matrix Elements	Barium % m/m		Zinc % m/m		Calcium % m/m		Phosphorus % m/m	
		Chem.	X-ray	Chem. <sup>3</sup>	X-ray	Chem.	X-ray	Chem. <sup>6</sup>	X-ray
A	2S	6.66	6.70 <sup>1</sup>	1.91	1.91	-	-	2.11	2.13
B	7Ba, 2Zn	-	-	-	-	-	-	1.80	1.91
C	4S, 2P	4.37	4.39 <sup>2</sup>	2.10	2.24	-	-	-	-
D	2S, 1P	7.56	7.43	1.67	1.68	-	-	-	-
E	7Ba, 3S, 1P	-	-	1.32	1.33	-	-	-	-
F	2S	3.26	3.30 <sup>2</sup>	-	-	-	-	-	-
G	16S, 8P	-	-	8.76	8.88	3.71	3.80	-	-
H	1Zn, 3S	7.09	7.13 <sup>1</sup>	-	-	-	-	-	-
I	16S, 8P	-	-	8.82	8.99	-	-	1.30	1.32
J	20S, 9P	-	-	10.56	10.61	-	-	-	-
K	17S, 8P	-	-	9.17	9.20	-	-	-	-
L	1Zn, 2S, 1P	12.13	12.21 <sup>2</sup>	-	-	-	-	-	-
M	-	2.60 <sup>1</sup>	2.41	1.22	1.23	2.00 <sup>4</sup>	2.07	-	-
N	-	-	-	1.16	1.17	2.45	2.66	-	-
O	1Zn	11.00 <sup>1</sup>	10.82	-	-	1.04	1.01	-	-
P	3An, 5S	-	-	-	-	2.66	2.71	2.60	2.78

\* excluding carbon and hydrogen

## Chemical Methods:

- Barium: 1. Volumetric method using EDTA and magnesium chloride  
 Barium: 2. IP110/82  
 Zinc: 3. Potentiometric method using potassium ferrocyanide  
 Calcium: 4. Volumetric method using EDTA and magnesium chloride  
 Calcium: 5. IP110/82  
 Phosphorus: 6. Volumetric method using potassium hydroxide

T A B L E 5

Analytical Data

Element Analytical line	Ba La	Zn Ka	Ca Ka	P Ka	Zr Ka	Zr La
Approx. count rate, cps/%	300	1500	600	1400	900	400
Background count rate, cps	2	64	245	5	80	3
Limit of detection*, %	0.01	0.02	0.04	0.01	0.03	0.01
Conc. range, µg/sq cm	0-150	0-150	0-80	0-50	10-20	10-20
Wet film thickness, µm	25	25	25	25	25	25
Dilution factor	3	3	3	3	3	3

\* The limit of detection was determined using  $\frac{3}{M} \sqrt{R/T}$ , where M is the slope of the line in cps/%, R is the background count recorded in time T found using a specimen in which the element sought was absent.

1) The Mylar film contained a small quantity of calcium.



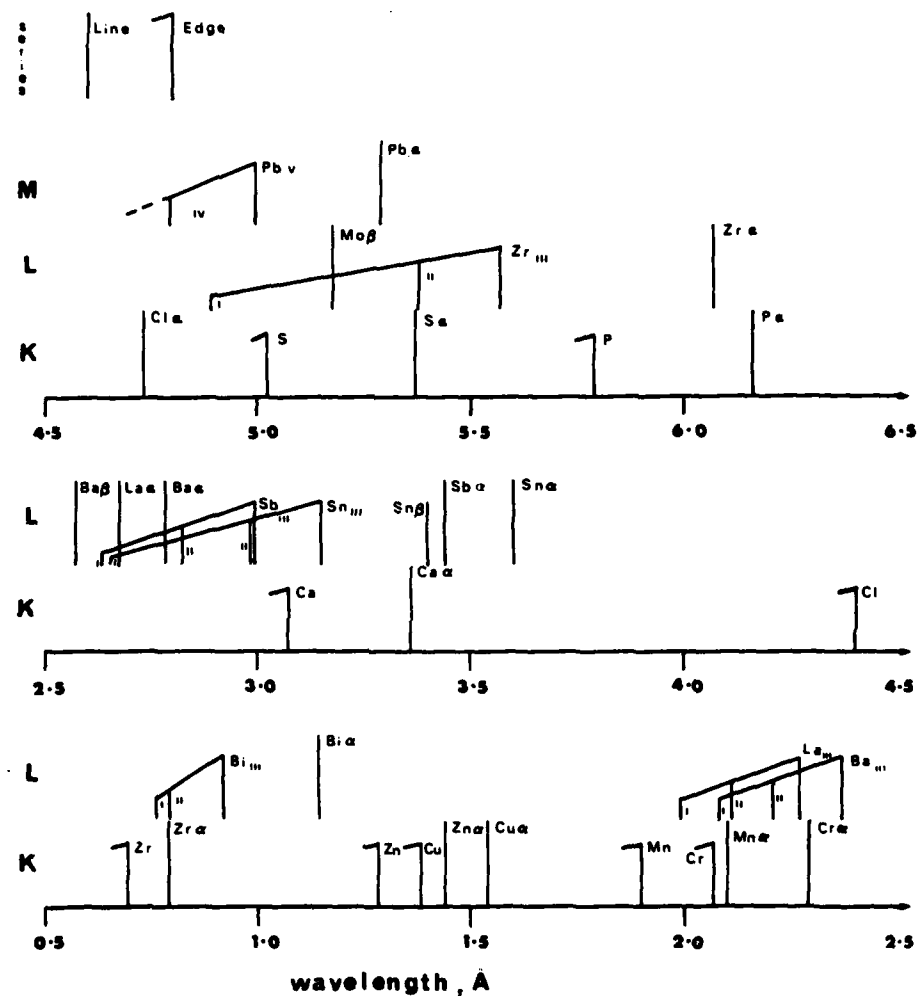


FIG. 1 Principal lines and edges of elements in additives together with elements useful as internal standards.



FIG. 2      Photograph of the K Hand Coater and impression bed used  
to prepare the thin films.

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